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Neutron Diffraction Study of the Irreversible R–M_A–M_C Phase Transition in Single Crystal $Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$

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Single crystals of the relaxor PZN–xPT display an enormously strong piezoelectric character. Recent x-ray scattering studies have revealed novel electric-field induced phase transitions in PZN–8%PT. As-grown crystals exhibit a rhombohedral structure that, under application of an electric field oriented along [001], transforms into a monoclinic (M_A) phase, and then irreversibly to another monoclinic (M_C) phase with increasing field strength. Since the latter phase change is very unusual, its transition sequence has been investigated by using triple-axis neutron scattering techniques so that the "skin effect" observed by x-ray scattering can be avoided, and the entire crystal bulk is probed. Contour maps of the elastic scattering have been mapped out in each phase in the (H0L) zone with high q-resolution. Increasing the field strength within the M_C phase induces a sharp c-axis jump around 15 kV/cm. This jump was observed easily with x-rays in previous studies, but it was not observed in 5 different crystals examined with neutrons. A subsequent high-energy x-ray study of the same crystals showed that the c-axis jump is distributed within the crystal volume, thereby washing out the jump. The observed R–M_A–M_C transformational path is in perfect accord with very recent first principles calculations by Bellaiche, Garcia, and Vanderbilt in the PZT system.

KEYWORDS: relaxor, ferroelectric, PZN–xPT, phase transition, electric field, neutron scattering

§1. Introduction

Several recent experimental and theoretical studies have significantly advanced our understanding of the origin of the exceptionally high piezoelectric and dielectric responses that have been reported in the lead-oxide class of relaxor ferroelectrics. The x-ray work by Noheda *et al.*[1,2] uncovered a previously unknown sliver of monoclinic (M) phase nestled against the morphotropic phase boundary (MPB) separating the rhombohedral (R) and tetragonal (T) regions of the phase diagram of $Pb(Zr_xTi_{1-x})O_3$ (PZT),[3] a perovskite system that is the material of choice in the fabrication of high performance actuators and transducers for industrial applications. Subsequent x-ray measurements have revealed the presence of a similar narrow region of monoclinic phase in the relaxor $Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3$ (PZN–xPT),[4,5] a ferroelectric material that exhibits an ultra-high strain in high field fully 10 times that of PZT.[6–8] In both PZN–xPT and PZT the maximum piezoelectric activity is located on the R side very near the MPB, thereby underscoring the important role played by the monoclinic phase.

These observations triggered the theoretical work of Fu and Cohen who introduced the concept of the polarization rotation mechanism to explain the ultra-high electromechanical response.[9] Whereas in the conventional ferroelectric phases of tetragonal $PbTiO_3$ and $BaTiO_3$ the polarization vector points along the [001] and [111] directions, respectively, the monoclinic symmetry afforded the PZT and PZN–xPT compounds near the MPB allows the polarization vector a much greater degree of freedom as it is only constrained to lie within a monoclinic plane defined by the pseudo-cubic [001] and [111] directions in the case of PZT, i.e., the $(1\bar{1}0)$ plane, and the [001] and [101] direction in the case of PZN–xPT, i.e., the (010) plane. In the monoclinic phase, the polarization direction can easily adjust to the electric field, which naturally results in a large piezoelectric response. A polarization rotation path within the $(1\bar{1}0)$ plane can be considered phenomenologically by expanding the Devonshire theory of ferroelectrics to eighth or higher order as done by Vanderbilt and Cohen.[10] Indeed, such an expansion allows for monoclinic phases in addition to R, T and orthorhombic (O) phases, and is able to generate a global phase diagram within eighth order.

PZN–xPT is a perovskite (ABO_3) solid solution of the relaxor $Pb(Zn_{1/3}Nb_{2/3})O_3$ ($T_c = 410$ K) and the ferroelectric $PbTiO_3$ ($T_c = 673$ K). The system has cubic symmetry at high temperatures and undergoes a diffuse ferroelectric phase transition above room temperature for low values of x,[6] which is strongly frequency-dependent (hence the term "relaxor"). This unusual diffuse phase transition is believed to be due to the

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complex mixture of Zn^{2+}, Nb^{5+}, and Ti^{4+} cations which give the perovskite *B*-site a marked mixed valence character. Unlike PZT, PZN–*x*PT can be grown in single crystal form which makes it possible to study their structural properties in detail.

Single crystals of PZN–*x*PT exhibit the greatest piezoelectric response for $x = 8\%$, which is located near the MPB on the R side.[8] Strain field loops for PZN–8%PT [see Fig. 1(a)] and PZN–4.5%PT, where the electric field was oriented along the pseudo-cubic [001] direction, show that the strain increases linearly below a threshold field, and then suddenly jumps,[8] an effect which is known as a *c*-axis jump. This threshold field, as well as the piezoelectric response, decreases as *x* increases beyond the MPB and into the tetragonal phase. X-ray scattering experiments on PZN–8%PT by Durbin *et al.* were able to reproduce this *c*-axis jump behavior.[11] In addition, Durbin *et al.* discovered that an irreversible change in phase takes place from the "as-grown" state to a different phase with the application of an electric field.[12] Subsequent x-ray measurements by Noheda *et al.* identified the proper symmetries of the various phases.[4] In particular, Noheda *et al.* showed that poled crystals have a monoclinic (M_C) symmetry that is different from that found in the PZT system (M_A).[4] Furthermore, it was shown that as-grown PZN–*x*PT crystals have a rhombohedral symmetry that transforms irreversibly upon application of an electric field along [001] to a monoclinic (M_C) phase via an intermediate monoclinic (M_A) phase.[4] This sequence is surprising as it runs counter to the theoretical sequence proposed by Fu and Cohen of R–M_A–T based on calculations performed for $BaTiO_3$.[9] Instead, it appears that the M_A phase is needed for the R–M_C phase transition.[4] Figure 1(b) depicts the path followed by the polarization rotation for the R–M_A–M_C phase sequence proposed.[4] These results are in excellent agreement with the first principles calculations done for the PZT system by Bellaiche *et al.*,[13] which were made public during the preparation of this manuscript.

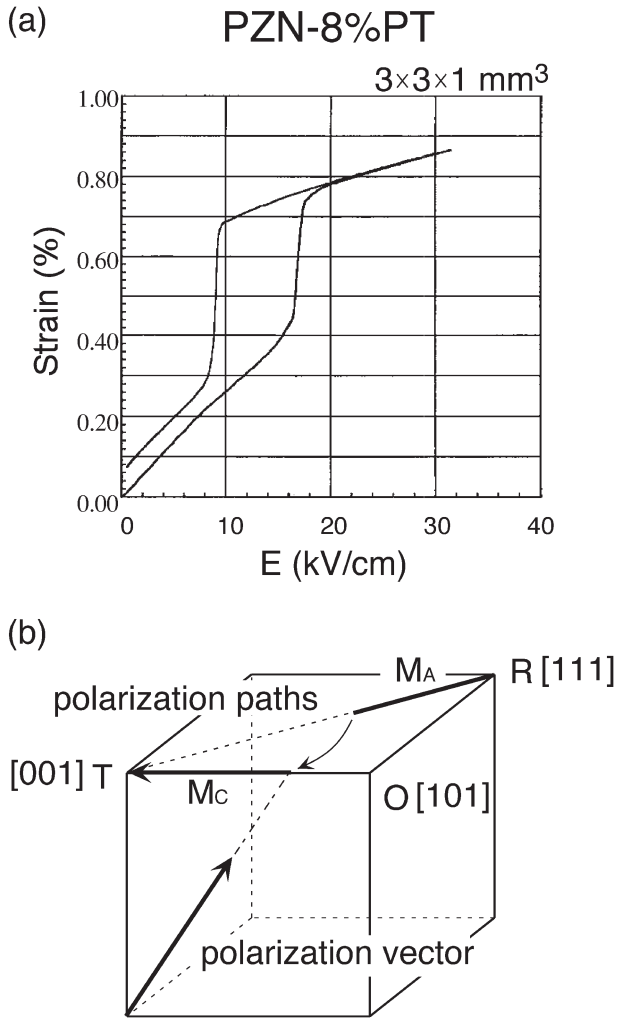

Fig. 1. (a) Electric field dependence of the strain measured on the $3 \times 3 \times 1$ mm^3 PZN–8%PT crystal (ref. 8). (b) Polarization path for the PZN–8%PT crystal.

It is now clear that PZN–8%PT shows two novel field-induced phase transitions. To clarify the origin of the exceptional piezoelectric character of this system, we have studied this complicated transformation sequence in detail. Discrepancies between recent x-ray and neutron scattering studies suggest that the near-surface region (or *skin*) of a single crystal of PZN–*x*PT may behave differently from the crystal bulk. We have thus carried out neutron scattering experiments under an applied electric field where we have made significant efforts to improve the instrumental *q* resolution.

§2. Experimental Details

Neutron scattering measurements have been performed on 5 different single crystals of 8.0%PT having dimensions $2 \times 2 \times 2$ mm^3 (two of them), $3 \times 3 \times 1$ mm^3, $6 \times 6 \times 3$ mm^3, and $8 \times 8 \times 2$ mm^3. Similar measurements were also performed on 2 single crystals of 4.5%PT with dimensions $2 \times 2 \times 0.5$ mm^3, and $3 \times 3 \times 1$ mm^3. The two $2 \times 2 \times 2$ mm^3 crystals were also used in the first x-ray diffraction study of 8.0%PT by Durbin *et al.*[11] These crystals were grown at Penn State University, and the strain curves measured along [001] as a function of electric field strength were always used as a gauge of crystal quality. As shown in Fig. 1, the $3 \times 3 \times 1$ mm^3 crystal exhibits a sharp jump in the *c*-axis lattice spacing around 15 kV/cm.

The neutron diffraction experiments were carried out at the JRR-3M reactor located at the Japan Atomic Energy Research Institute (JAERI) in Tokai. Additional measurements were performed at the NBSR reactor located at the NIST Center for Neutron Research in Gaithersburg, Maryland. A very high instrumental *q*-resolution of 0.003 Å^{-1} full-width half maximum (FWHM) was achieved by using a perfect Ge (220) crystal as analyzer. The (220) Bragg planes of Ge have a *d*-spacing of 2.0 Å, a value that closely matches that of the (200) Bragg planes of the PZN–*x*PT perovskite oxides. This technique of lattice matching results in a high *q*-resolution. The same method was used in prior high resolution studies of $CuGeO_3$.[14]

A supplemental high-energy x-ray study was performed at the superconducting-wiggler beam line X17B located at the National Synchrotron Light Source

(NSLS) at Brookhaven National Laboratory in Upton, New York. X-rays of this energy can pass through a 3 mm thickness of PZN and permits the study of cross sections as small as 50 microns.

§3. The Irreversible Structural Phase Transformation Sequence R–M_A–M_C

To study the R–M_A–M_C phase transition sequence, contour maps of the elastic scattering have been mapped out in each phase in the (H0L) zone around the (200) reciprocal lattice position with high q-resolution as a function of electric field applied along the [001] direction. These data are shown in Fig. 2, and were taken on an $8 \times 8 \times 2$ mm^3 PZN–8%PT crystal that had been poled in a field of 15 kV/cm along [001] (i.e., normal to the 8×8 mm^2 crystal surface). The contour maps provide an extremely useful two-dimensional view of the scattering associated with each phase. The scattering intensity has been represented on a logarithmic gray scale as shown in the inset of Fig. 2(b). Our measurements began with the poled crystal at room temperature (RT) and in zero applied field. In this state, a domain structure is found in which the (200) peak is split and the (020) peak is clearly observed [see Fig. 2(a)]. The a and c lattice constants are nearly equal, but the b-axis spacing is noticeably smaller. This suggests that the polarization direction lies in the ac-plane, and that the crystal is indeed in the M_C-phase as a result of the poling. The data shown in Fig. 2(a) are consistent with the x-ray results on PZN–8%PT obtained by Noheda *et al.*[4] Next, the crystal was warmed above 500 K to restore it to the cubic (C) phase. The result is a single sharp peak near (200) (slightly shifted due to the thermal expansion) as shown in Fig. 2(b). The (20L) scattering profile for each of these two phases is shown in Fig. 3(a) for comparison. The cubic phase profile is exceedingly sharp, reflecting the relaxation of the local strains by thermal fluctuations. The crystal was then cooled to RT, whereupon the phase becomes R, as is observed in other crystals in their as-grown state at RT [Fig. 2(c)]. The substantially broadened peak width suggests the generation of local distortions caused by the randomly-oriented ⟨111⟩ polar nanoregions (PNR).

An electric field was first applied to the crystal in the R phase, after cooling from 500 K to RT. From this point on, all data were taken at room temperature. Immediately after $E = 0$ kV/cm, the rhombohedral phase transformed into the M_A phase. This is shown in Fig. 2(d) for $E = 5$ kV/cm. We also display the electric field dependence of the c-axis lattice constant and the observed monoclinic angle in Fig. 3(c) and 3(d). From Fig. 2(c) we see that the (200) peak splits into two peaks

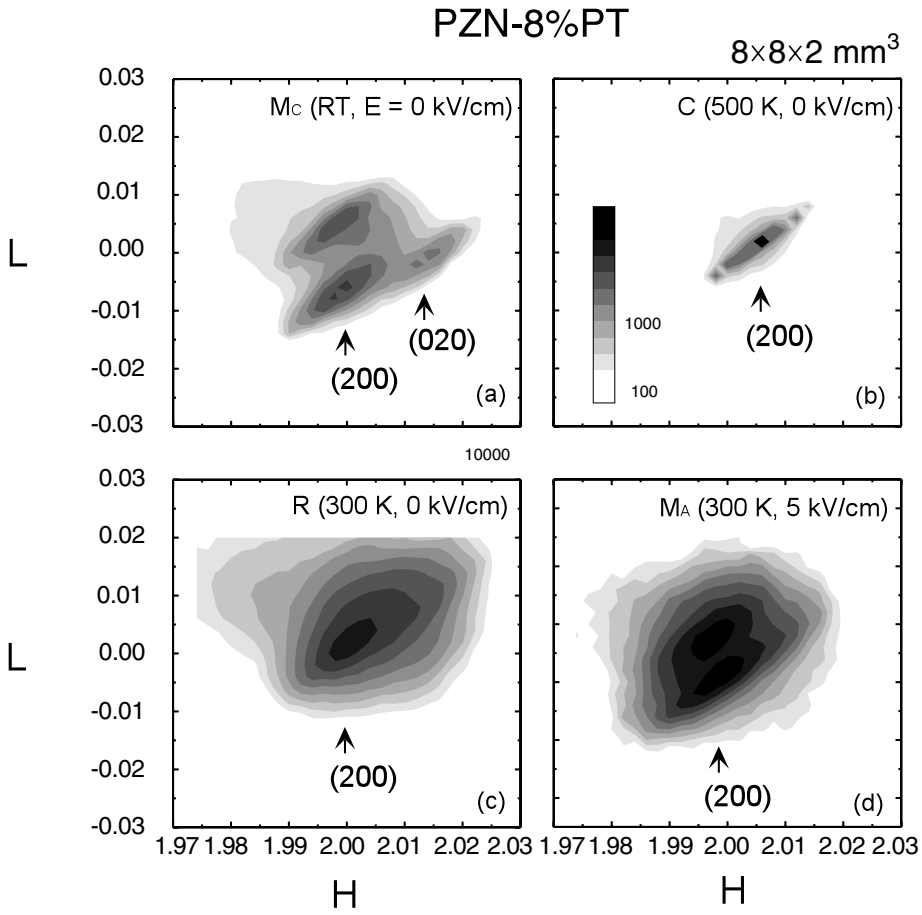

Fig. 2. Contour maps of the (H0L) zone around (200) showing the sequence of phase transitions observed in the PZN–8%PT ($8 \times 8 \times 2$ mm^3 crystal as a function of temperature and electric field. (a) M_C-phase at RT and $E = 0$ kV/cm, (b) C-phase at $T = 500$ K and $E = 0$ kV/cm, (c) R-phase at $T = 300$ K and $E = 0$ kV/cm, (d) M_A-phase at $T = 300$ K and $E = 5$ kV/cm.

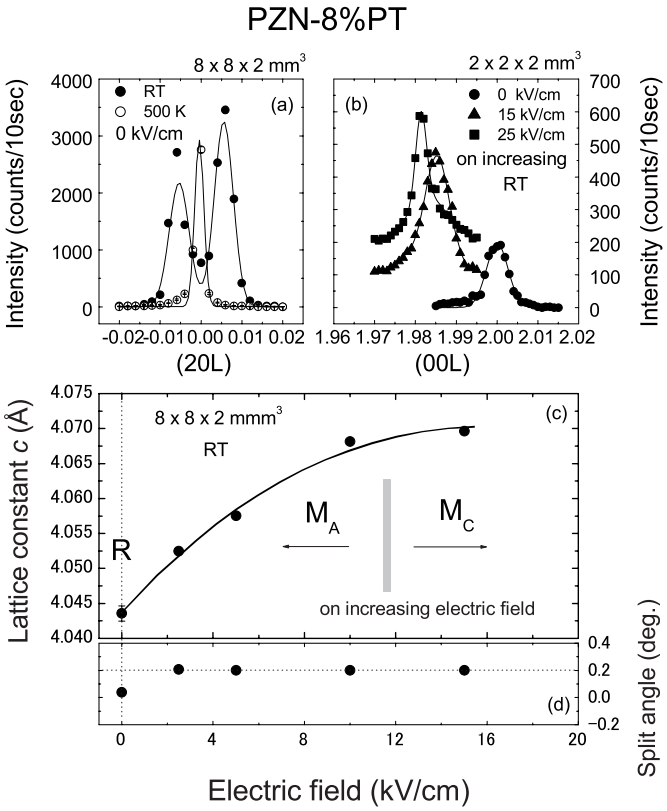

Fig. 3. (a) (20L) peak profiles in the M_C (solid circles) and C (open circles) phases of the PZN–8%PT $8 \times 8 \times 2$ mm^3 crystal. (b) Electric field dependence of the (00L) peak profiles taken at several fields 0, 15, 25 kV/cm. (c) Lattice constant c and (d) peak split angle as a function of electric field taken at the R–M_A–M_C transition sequence. Solid lines drawn through the data points are guides to the eyes.

at 5 kV/cm, however no other peaks appear. This suggests that the polarization direction is oriented between $\langle 111 \rangle$ and $\langle 001 \rangle$, and thus corresponds to the M_A-phase. The angle formed by the two split peaks is about 0.2° [see Fig. 3(d)] and is independent of electric field in the M_A-phase. The appearance of the (020) peak signals the M_A–M_C phase transition, and is attained between $E = 10$ and 15 kV/cm. The M_C phase is retained as the ground state structure of the PZN–8%PT crystal, even after removal of the applied field. This is demonstrated by Fig. 2(a) which depicts the state of the crystal after poling along [001] in a field of 15 kV/cm. The R phase, by contrast, is not recovered at $E = 0$ kV/cm, hence the transition to the M_C phase is irreversible.

We examine the electric field dependence of the c-axis lattice constant more closely in a second crystal ($2 \times 2 \times 2$ mm^3), poled such that it is in the M_C phase, in the next section.

§4. The c-axis Jump

The search for the c-axis jump using neutron scattering techniques grew out of our initial attempts to study the effects of an applied electric field on the soft phonon anomalies reported in PZN–8%PT by Gehring *et al.*[15] During these measurements it was noted that the c-axis jump observed with x-rays by Durbin *et al.*[11] was missing. The magnitude of the jump in the c-axis spacing is of order 0.5%, and so should have been clearly visible with neutron scattering techniques. The discrepancy between neutron and x-ray scattering results stimulated a much more intensive search for the c-axis jump, and involved the study of a total of 5 different single crystals, including two $2 \times 2 \times 2$ mm^3 crystals that were used in the x-ray study. Nevertheless the c-axis jump was not reproduced in the neutron scattering data. The absence of the c-axis jump in the neutron experiments suggested that the outer volume, or "skin" of the crystals could be behaving differently from the crystal interior given that the x-rays and neutrons probe different volumes of the crystal. The x-rays used by Durbin *et al.* were obtained from a Cu K_α rotating anode source with a wavelength $\lambda = 1.541$ Å (8 keV), and penetrate only of order 1 μm ($1\,\mu\text{m} = 10,000$ Å) into the crystal due to the high lead content of these samples. Neutrons, by contrast, probe the entire crystal volume. This idea prompted a subsequent x-ray study by Noheda *et al.* using much higher energy x-rays (67 keV) in which it was shown that so-called "skin effects" are in fact important in these lead-oxide relaxor systems.[4] Figure 4 shows the results obtained using high-energy x-rays on crystals of PZN–8%PT. The scattering that occurs from mainly the surface (upper panel) and the bulk (lower panel) reveal that the sharp c-axis jump is in fact distributed over the crystal volume, thereby effectively washing out the c-axis jump. Motivated by this x-ray work, we carried out a new series of neutron scattering measurements under an applied electric field with a significantly higher q-

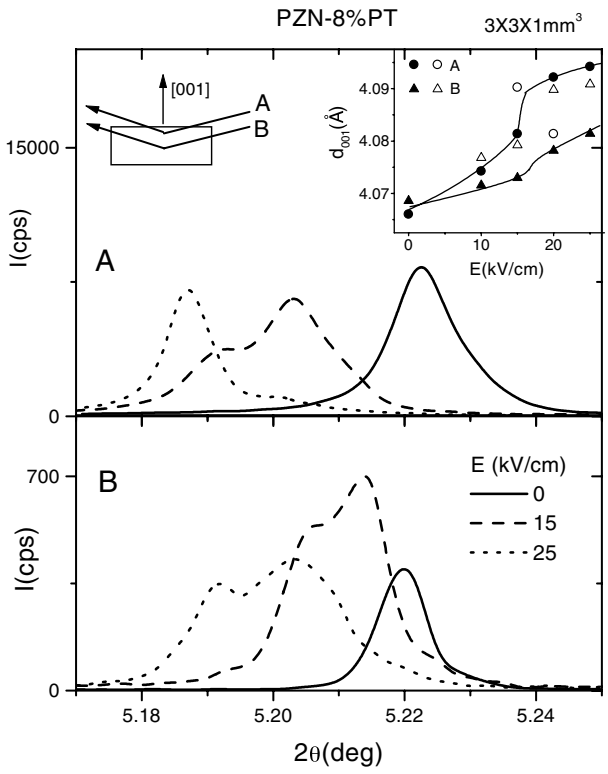

Fig. 4. High-energy x-ray results on PZN–8%PT crystals showing the c-axis jump is distributed within the crystal volume. Diffraction patterns resulting mainly from the surface (bulk) are shown in the upper (lower) panel. The evolution of the spacing of the 001 plane d_{001} with the electric field is shown in the inset for both surface (A) and the bulk (B). The major (minor) component in the diffraction peaks is represented as solid (open) symbols.

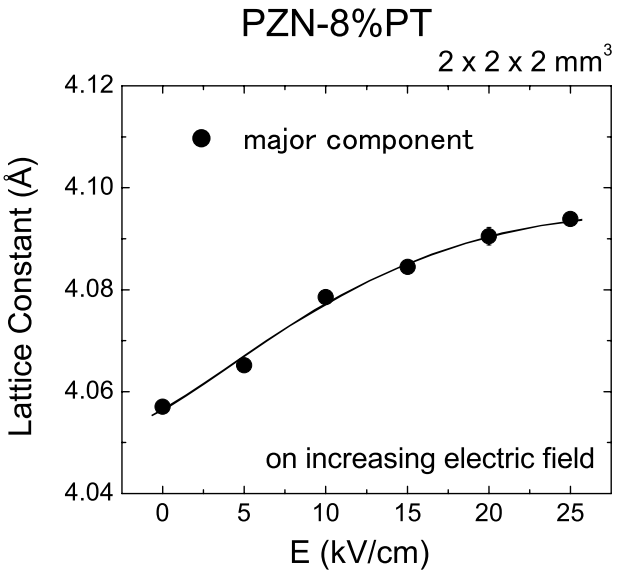

Fig. 5. Electric field dependence of the c-axis lattice constant of PZN–8%PT measured with increasing field. The solid circles represent the major component of the peak profiles. The solid line is a guide for the eyes. There is no sharp jump as was seen in Fig. 1(a).

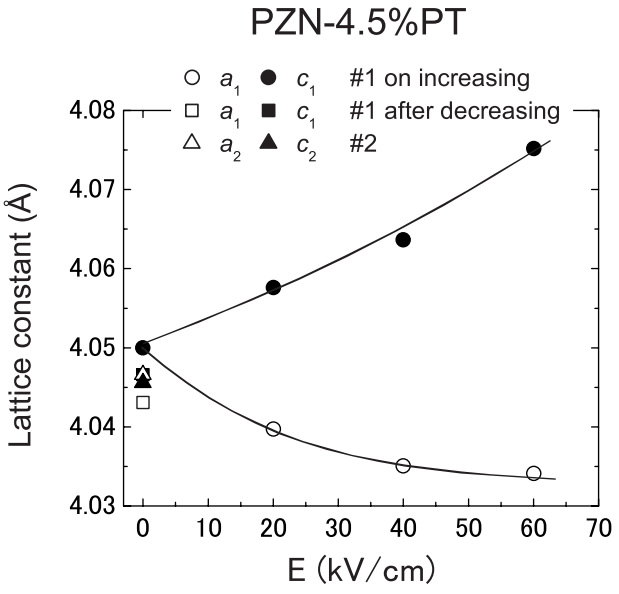

Fig. 6. Electric field dependence of the lattice constant a and c of PZN–4.5%PT measured on increasing field. The solid line is guided for the eyes. There is also no jump as reported in ref 16.

resolution than before.

Selected $(00L)$ peak profiles at $E = 0.0$, 15.0 and 25.0 kV/cm are shown in Fig. 3(b). The important feature to note is the asymmetry of the peak profiles due to the shoulder exhibited on the low-q side at $E = z15$ kV/cm, and then on the high-q side at $E = 25$ kV/cm. This asymmetry is a measure of the strain distribution present throughout the crystal because neutrons probe the entire crystal volume. More importantly, this asymmetry demonstrates that the strain is not uniform within the crystal. In addition, the peak profile sharpens with increasing field. These results are consistent with the previous high-energy x-ray results of Noheda *et al.*,[4] and confirm the presence of the distributed phase transition. By extracting the peak position of the major component of the measured profiles, one obtains the field dependence of the c-axis lattice constant shown in Fig. 5. The c-axis gradually expands and shows no jump around the threshold field of 16 kV/cm. For comparison, the experimental results obtained at the NIST Center for Neutron Research on a single crystal of PZN–4.5%PT are shown in Fig. 6. Again, there is no jump at its threshold field of 35 kV/cm.[16] These results indicate that the strain is distributed throughout the crystal volume, and thus provides a natural explanation for why neutron scattering, which is a bulk probe, does not observe a sharp c-axis jump.

§5. Conclusion

Neutron scattering experiments have been carried out with very sharp q-resolution on single crystals of the highly piezoelectric relaxor material PZN–xPT as a function of applied electric field. Contour plots of the elastic scattering measured in the (H0L) zone near the (200) Bragg peak in PZN–8%PT confirm the irreversible R–M_A–M_C sequence of transformations first reported in the x-ray studies of Durbin and Noheda.[4,11] While the presence of a monoclinic phase in a cubic perovskite ferroelectric system is quite unusual, it can now be

understood within the framework of an extended Devonshire theory for strongly anharmonic crystals for which higher order terms become important.[10] However, the actual path taken by the polarization in PZN–8%PT under the influence of an applied electric field was unexpected. The first principles calculations performed by Fu and Cohen[9] on $BaTiO_3$ suggest that the R–T path should be the most energetically favorable one. This has turned out not to be the case as instead the system crosses over from the R–T to the O–T path indicated in Fig. 1, resulting in the appearance of the M_C phase. In addition, the first principles calculations of Bellaiche, Garcia, and Vanderbild predict the R–M_A–M_C–T transformation to be reversible upon removal of the electric field.[13] This is not observed experimentally in PZN–8%PT.

The electric field dependence of the lattice strain of a poled PZN–8%PT crystal measured along the field direction has also been studied. The sharp jump in the *c*-axis lattice spacing previously observed with x-rays was not reproduced by our neutron experiment. Instead, a marked asymmetry of the (002) Bragg peak line shapes measured along the *c*-axis is observed, and is ascribed to a non-uniform strain distribution within the crystal that in turn leads to distributed *c*-axis jumps throughout the crystal volume to the high-field tetragonal (T) phase. These results are consistent with previous experimental observations using low and high-energy x-rays, and demonstrate the important finding that the responses of the skin (surface) and bulk (inner volume) regions of the crystal are different in these piezoelectric materials.

Acknowledgments

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